

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

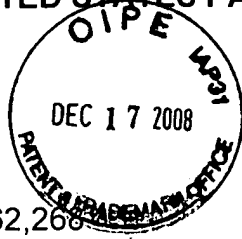
In re Application of:

KAWAGUCHI et al.

Application No.: 10/562,266

Filed: December 28, 2005

Title: ALKALI-FREE GLASS



) Examiner: Elizabeth A. Bolden

) Group Art Unit: 1793

) Confirmation No.: 8212

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Commissioner for Patents

U.S. Patent and Trademark Office

Alexandria, VA 22314

SUBMISSION OF VERIFIED TRANSLATION OF PRIORITY DOCUMENT

Sir:

In connection with the Response to the Official Action dated September 17, 2008, filed concurrently herewith, Applicants respectfully submit a verified translation of JP 2003-205812

Respectfully submitted,

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PATENT APPLICATION
IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of

Masataka KAWAGUCHI, et al.

Appln. No.: 10/562,268

Group Art Unit: 1793

Filed: December 28, 2005

Examiner: BOLDEN, ELIZABETH A

For: ALKALI-FREE GLASS

STATEMENT

Assistant Commissioner for Patents
Alexandria, VA 22313-1450

Sir/Madam:

I, Koji Yokokawa, residing at 37-10, Shimizu 1-chome, Suginami-ku,
Tokyo, Japan hereby state that:

I well understand the Japanese and English languages and attached is
an accurate English translation made by me of Japanese Patent Application No.
2003-205812, filed August 4, 2003.

Date: December 16, 2008 Name: Koji Yokokawa
Koji YOKOKAWA



[Designation of Document] Specification

[Title of the Invention] ALKALI-FREE GLASS

[Claims]

[Claim 1] An alkali-free glass which comprises: by mass %,

5 SiO_2 in an amount of from 40 to 70%;

Al_2O_3 in an amount of from 6 to 25%;

B_2O_3 in an amount of from 5 to 20%;

MgO in an amount of from 0 to 10%;

CaO in an amount of from 0 to 15%;

10 BaO in an amount of from 0 to 30%;

SrO in an amount of from 0 to 10%;

ZnO in an amount of from 0 to 10%, and

 helium and/or neon in an amount of from 0.0001 to 2
 $\mu\text{l/g}$ (0°C, 1 atm.).

15 [Claim 2] The alkali-free glass according to claim 1,
which further comprises a fining component.

[Claim 3] The alkali-free glass according to claim 2,
wherein the fining component is at least one selected from
the group consisting of SO_3 , Sb_2O_3 , SnO_2 and Cl_2 .

20 [Claim 4] The alkali-free glass according to claim 3,
wherein SO_3 is contained in an amount of from 0.0001 to
0.03%.

[Claim 5] The alkali-free glass according to claim 3,
wherein Sb_2O_3 is contained in an amount of from 0.05 to 3%.

25 [Claim 6] The alkali-free glass according to claim 3,

wherein SnO_2 is contained in an amount of from 0.05 to 1%.

[Claim 7] The alkali-free glass according to claim 3,
wherein Cl_2 is contained in an amount of from 0.005 to 1%.

[Claim 8] A transparent glass substrate for a liquid
5 crystal display which is obtainable by the alkali-free
glass according to any one of claims 1 to 7.

[Detailed Description of the Invention]

[Technical Field to which the Invention Belongs]

The present invention relates to an alkali-free glass,
10 particularly an alkali-free glass utilized as a transparent
glass substrate for a liquid crystal display.

[Related Art]

An alkali-free glass is employed as a transparent
glass substrate for a liquid crystal display or the like.
15 Such alkali-free glass is required to be free from bubbles
constituting defects in the display.

The alkali-free glass is melted at a higher
temperature in comparison with glass containing an alkali
metal component, because of a high viscosity of the molten
20 glass. In melting the alkali-free glass, a vitrifying
reaction usually takes place at from 1200 to 1400°C, and
bubble reduction and homogenization are executed at a high
temperature of 1500°C or higher. Therefore, it is
necessary to utilize a fining agent capable of releasing
25 fining gas at least in a high temperature region where the

bubble reduction and the homogenization are executed.

Because of such situation, As_2O_3 capable of generating fining gas in a wide temperature range has been widely employed as the fining agent for the alkali-free glass.

5 However, As_2O_3 is a hazardous material and it is desired to reduce or totally replace such material.

Therefore, methods utilizing SO_3 , Sb_2O_3 , SnO_2 , Cl_2 or the like as an alternative fining agent for As_2O_3 are proposed (for example, patent references 1 and 2).

10 [Patent Reference 1]

JP-A-11-43350

[Patent Reference 2]

JP-A-2000-159541

[Problems that the Invention is to Solve]

15 The alternative fining agent mentioned above has enabled to bring a number of bubble inclusion, called seed, of the glass to a practically acceptable level, but fewer bubble inclusion is required along with a recent increase in the size of the liquid crystal display screen.

20 An object of the present invention is to provide an alkali-free glass which is capable of reducing or totally eliminating As_2O_3 and which has fewer bubble inclusion than that in the prior technology.

[Means for Solving the Problems]

25 The present inventors have found that bubbles in the

molten glass can be completely eliminated or significantly reduced by including a specific amount of an inert gas component such as helium or neon, as a component providing a fining effect in the alkali-free glass, in the molten
5 glass and have thus made the present invention.

More specifically, an alkali-free glass of the present invention comprises: by mass %,

SiO₂ in an amount of from 40 to 70%;
Al₂O₃ in an amount of from 6 to 25%;
10 B₂O₃ in an amount of from 5 to 20%;
MgO in an amount of from 0 to 10%;
CaO in an amount of from 0 to 15%;
BaO in an amount of from 0 to 30%;
SrO in an amount of from 0 to 10%;
15 ZnO in an amount of from 0 to 10%, and
helium and/or neon in an amount of from 0.0001 to 2
μl/g (0°C, 1 atm.). In the invention, "alkali-free" means
that alkali metal oxides (Li₂O, Na₂O, and K₂O) are present
in an amount of 0.2% by mass or less.

20 The alkali-free glass according to the present invention may further comprises a fining component.

In the alkali-free glass according to the present invention, the fining component may be at least one selected from the group consisting of SO₃, Sb₂O₃, SnO₂ and
25 Cl₂.

In the alkali-free glass according to the present invention, SO_3 may be contained in an amount of from 0.0001 to 0.03%.

In the alkali-free glass according to the present invention, Sb_2O_3 may be contained in an amount of from 0.05 to 3%.

In the alkali-free glass according to the present invention, SnO_2 may be contained in an amount of from 0.05 to 1%.

10 In the alkali-free glass according to the present invention, Cl_2 may be contained in an amount of from 0.005 to 1%.

A transparent glass substrate for a liquid crystal display of the present invention is obtainable by the
15 above-mentioned alkali-free glass.

[Mode for Carrying Out the Invention]

In the molten glass, the elements form a network state of a weak bonding force, and show irregular relative positional changes involving elongational, rotational and
20 angular vibrations more vigorously at a higher temperature. However, helium or neon, because of a closed-shell structure of the electrons in the atomic structure, shows a very low reactivity and a small dimension, as will be explained later. Therefore, helium or neon, scarcely
25 binding with the elements constituting the molten glass and

having a sufficiently small dimension capable of passing through a gap in the vibrating network mentioned above, can easily diffuse into a bubble present as a defect in the molten glass, without being affected by the surrounding
5 elements.

Therefore, by contacting helium or neon with the molten glass including a plurality of fine bubble defects, it is possible to rapidly expand the size of the fine bubbles incorporated in the molten glass. As a result, the
10 bubbles with an expanded size show a larger floating power and float rapidly, whereby the molten glass is promptly fined. Helium or neon thus provides a fining effect in the molten glass, and such effect is enhanced in a condition where the molten glass contains various fining agents to be
15 explained later. This is because, in addition to the fining effect of helium or neon itself and the fining effect of the various fining agents, a multiplying effect is obtained by diffusion of helium or neon in fine bubbles generated by the various fining agents.

20 Helium or neon to be employed in the invention, being classified as inert gas or rare gas and having a stable closed shell structure, is present in the state of a single-atom molecule. Helium is the lightest element among the rare gases, shows a very small dimension in structure
25 and a very weak Van der Waals attractive force, and remains

in a liquid phase even at the absolute zero temperature without solidifying under an atmospheric pressure. Neon has a smaller dimension next to helium among the rare gases, and assumes a stable structure in a single-atom molecule as
5 in the case of helium. Therefore, in a glass composition prepared by melting at a high temperature following by cooling, helium or neon is present in a state trapped in a pore of a glass network structure constituted by other components.

10 Helium and/or neon is not involved in the formation of the glass network structure, but an amount of 0.0001 $\mu\text{l/g}$ or higher singly or in a united amount in the glass provides a fining effect. When it is less than 0.0001 $\mu\text{l/g}$, it is impossible to give a sufficient fining effect. Also
15 an amount of 0.06 $\mu\text{l/g}$ or higher enables a secure fining effect. Also for realizing a fining effect even under a severe condition wherein the glass has a higher content of gasifyable components, there is more preferred a content of 0.1 $\mu\text{l/g}$ or higher which provides the molten glass with a
20 sufficient fining effect. On the other hand, a content of more than 2 $\mu\text{l/g}$ is undesirable because it generates re-boiling, when the glass composition is heated again. An upper limit content not causing the re-boiling is preferably 1.5 $\mu\text{l/g}$ or less, though it is variable
25 depending on a glass composition and a heating condition.

Such upper limit of 1.5 $\mu\text{l/g}$ is shifted lower to 1.0 $\mu\text{l/g}$ in case of a glass composition also comprising a fining agent other than helium and/or neon, since the re-boiling is facilitated.

5 Therefore, following ranges are preferred for the content of helium and neon. When the glass composition does not comprise a fining agent other than helium and neon, a content range providing the fining effect even under a severe condition and not easily causing the re-boiling is
10 preferably 0.1 to 1.5 $\mu\text{l/g}$. On the other hand, when the glass composition comprises a fining agent in addition to helium and neon, the range is preferably 0.1 to 1.0 $\mu\text{l/g}$.

Helium or neon can be added to the glass composition of the invention for example by a method of utilizing a
15 substance containing helium or neon at a high concentration or glass cullets containing helium or neon as a raw material, a method of melting the raw materials in a helium- or neon-containing atmosphere, or a method of contacting molten glass with a helium- or neon-containing
20 atmosphere.

For contacting the molten glass with a helium- or neon-containing atmosphere, there can be employed a method of introducing helium or neon into a container of molten glass, melting glass in a container with a gas permeability
25 and maintaining a helium- or neon-containing atmosphere

around the container, or a method of bubbling helium or neon with a refractory nozzle. In case of bubbling, a porous refractory material employed at an end of the nozzle facilitates efficient diffusion of helium or neon into the
5 glass.

The alkali-free glass of the present invention preferably comprises at least one selected from the group consisting of SO_3 (sulfate), Sb_2O_3 , SnO_2 and Cl_2 (chloride) as a fining agent component in addition to helium and/or
10 neon in the aforementioned range. The content of the fining agent as a remaining amount in the glass is preferably 0.0001 to 0.03% for SO_3 , 0.05 to 3% for Sb_2O_3 , 0.05 to 1% for SnO_2 and 0.005 to 1% for Cl_2 individually.

The fining agents mentioned above may be employed
15 singly, but are preferably employed in a combination of two or more thereof in order to obtain a higher fining effect. A combination of the fining agents includes following examples:

- (1) SO_3 in an amount of from 0.0001 to 0.03% and SnO_2 in
20 an amount of from 0.05 to 1%;
- (2) Sb_2O_3 in an amount of from 0.05 to 3% and SnO_2 in an amount of from 0.05 to 1%;
- (3) Sb_2O_3 in an amount of from 0.05 to 3% and Cl_2 in an amount of from 0.005 to 1%;
- 25 (4) Sb_2O_3 in an amount of from 0.05 to 3%, SnO_2 in an

amount of from 0.05 to 1% and Cl_2 in an amount of from 0.005 to 1%;

(5) SO_3 in an amount of from 0.0001 to 0.03% and Cl_2 in an amount of 0.005 to 1%; and

5 (6) SnO_2 in an amount of from 0.05 to 1% and Cl_2 in an amount of from 0.005 to 1%.

Each fining agent mentioned above exhibits a high fining effect by being present with helium and/or neon, and remains partly in the glass composition after cooling even
10 if it is denatured by a pyrolysis or an oxidation-reduction reaction in high-temperature melting.

A sulfate decomposes at a temperature range of about 1200 to 1500°C, and generates a large amount of fining gas (sulfur dioxide, oxygen gas) upon decomposition. SO_3
15 decomposes at a high temperature of 1400°C and is optimum for a glass having a vitrifying process at a high temperature, such as alkali-free glass. More specifically, SO_3 functions effectively as a fining agent in case of melting glass having a temperature, corresponding to a
20 viscosity of $10^{2.5}$ dPa.s, of 1500°C or higher. However, solubility of SO_3 in glass decreases with a decrease in the alkali content, and it is very low in case of an alkali-free glass. Stated differently, SO_3 releases a large amount of gas in the vitrifying process, but the fining
25 effect is reduced in a fining step after the vitrification

since SO_3 remains in a smaller amount therein.

Sb_2O_3 and SnO_2 release a large amount of fining gas (oxygen gas) by a chemical reaction involving a change in valence number of Sb ion and Sn ion. More specifically,

5 Sb_2O_3 (trivalent) once changes to Sb_2O_5 (pentavalent) at a low temperature range of several hundred degrees and releases a large amount of fining gas upon returning to Sb_2O_3 (trivalent) at about 1200 to 1300°C. Therefore the gas generated in the vitrifying process of the alkali-free

10 glass can be expelled from the molten glass. Also SnO_2 (tetravalent) releases a large amount of fining gas upon changing to SnO (divalent) at 1400°C or higher, and exhibits its effect at a homogenizing melting at a higher temperature.

15 A chloride decomposes and evaporates in a temperature range of 1200°C or higher to generate fining gas (chlorine gas etc.), and, showing vigorous decomposition and evaporation in a high temperature range of 1400°C or higher to generate a large amount of chlorine gas, is effect for

20 fining at a homogenizing melting.

Therefore, a combination of the fining agents having different temperature ranges for generating the fining gas enables to generating a fining gas over a wide temperature range from the vitrifying reaction at a relatively low

25 temperature to the homogenizing melting at a high

temperature, and achieves an even higher fining effect by the presence of helium and/or neon at the same time.

The fining agent is not particularly restricted in a method of addition, and may be added to a glass batch or
5 may be added later to the molten glass. Otherwise it may be added at the same time as the addition of helium or neon. It is also possible to add the aforementioned component into the molten glass as an eluting component from a container at the melting or a refractory material immersed
10 in the molten glass. It is furthermore possible to obtain an optimum addition amount by adding the fining agent alternately with helium or neon or by gradually increasing or decreasing the amount of addition under confirmation of the fining effect.

15 In the following there will be explained components other than the fining component in the alkali-free glass of the invention.

SiO_2 is a component constituting a network of the glass, and is present in an amount of from 40 to 70%,
20 preferably from 45 to 65%. When the amount of SiO_2 is less than 40%, chemical resistance becomes deteriorated and a strain point becomes lower to deteriorate heat resistance. While, when the amount thereof is more than 70%, a viscosity at a high temperature is increased to thereby
25 deteriorate melting property, and a devitrifying substance

such as cristobalite tends to precipitate easily.

Al_2O_3 is a component improving a heat resistance and a devitrification resistance of the glass, and is present in an amount of from 6 to 25%, preferably from 10 to 20%.

- 5 When the amount of Al_2O_3 is less than 6%, a devitrifying temperature is significantly increased and a devitrifying substance tends to generate easily in the glass. While, when the amount thereof is more than 25%, an acid resistance, especially a resistance to buffered
- 10 hydrofluoric acid becomes deteriorated, whereby a white turbidity tends to generate easily on the glass surface.

- B_2O_3 is a component functioning as a flux and reducing viscosity thereby facilitating melting, and is present in an amount of from 5 to 20%, preferably from 6 to
- 15 15%. When the amount of B_2O_3 is less than 5%, a sufficient effect as the flux can not be obtained. Moreover, when the amount thereof is more than 20%, resistance to hydrochloric acid is lowered and a strain point becomes low to deteriorate heat resistance.

- 20 MgO is a component reducing the viscosity at high temperature without lowering the strain point thereby facilitating the glass melting, and is present in an amount of from 0 to 10%, preferably from 0 to 7%. When the amount of MgO is more than 10% or less, resistance of glass to
- 25 buffered hydrofluoric acid becomes significantly

deteriorated.

CaO functions similarly as MgO, and is present in an amount of from 0 to 15%, preferably from 0 to 10%. When the amount of CaO is more than 15%, resistance of glass to buffered hydrofluoric acid becomes significantly deteriorated.

BaO is a component elevating the chemical resistance and improving the devitrifying property, and is present in an amount of from 0 to 30%, preferably from 0 to 20%. When the amount of BaO is more than 30%, a strain point becomes low to thereby deteriorating heat resistance.

SrO has an effect similar to that of BaO, and is present in an amount of from 0 to 10%, preferably from 0 to 7%. When the amount of SrO is more than 10%, it is not preferable because a devitrifying property is increased.

ZnO is a component improving a resistance to buffered hydrofluoric acid and a devitrifying property, and is present in an amount of from 0 to 10%, preferably from 0 to 7%. When the amount of ZnO is more than 10%, devitrification of the glass tends to generate easily, and a strain point becomes lowered and thus a good heat resistance cannot be obtained.

A total amount of MgO, CaO, BaO, SrO and ZnO is preferably from 5 to 30%. When the amount is less than 5%, a viscosity at a high temperature is increased to thereby

deteriorate a melting property, and devitrification of the glass tends to generate easily. On the other hand, when the amount thereof is more than 30%, it is not preferable because heat resistance and acid resistance are
5 deteriorated.

In addition to the foregoing components, ZrO_2 , TiO_2 , Fe_2O_3 etc. may be added up to 5% in a total amount.

In the following, a method for producing the alkali-free glass of the present invention will be described.

10 At first, there is a prepared glass batch so as to obtain a glass of the aforementioned composition. In case of introducing helium or neon, raw materials prepared correspondingly in advance are used. Also in case of using a fining agent such as SO_3 , Sb_2O_3 , SnO_2 , or Cl_2 , there may
15 be added a sulfate, Sb_2O_3 , SnO_2 , or a chloride to the glass batch. As a sulfate, $BaSO_4$, $CaSO_4$ etc. may be utilized. Also as a chloride, $BaCl_2$, $SrCl_2$, $CaCl_2$ etc. may be utilized.

An amount of the sulfate is preferably from 0.005 to 1% by mass in calculation as SO_3 based on 100% by mass of
20 the glass batch, and such amount of addition provides SO_3 of from 0.0001 to 0.03% in the glass. When the amount of sulfate is less than 0.005%, the gas generated in the vitrifying process is difficult to expel. While, when the amount thereof is more than 1%, it is easy to cause re-
25 boiling, whereby bubbles tends to remain in the glass. A

preferred amount of the sulfate is preferably from 0.01 to 1% in calculation as SO_3 , more preferably from 0.05 to 1% and further preferably from 0.05 to 0.5%. A preferred amount of SO_3 is from 0.0001 to 0.03%, more preferably from 0.0005 to 0.03%, and further preferably from 0.0005 to 0.01%.

An amount of Sb_2O_3 is preferably from 0.01 to 3% by mass based on 100% by mass of the glass batch. When the amount of Sb_2O_3 is less than 0.01%, the gas generated in the vitrifying process is difficult to expel. While, when the amount thereof is more than 3%, devitrification of the glass easily occurs. A more preferred amount of Sb_2O_3 is from 0.05 to 2%.

An amount of SnO_2 is preferably 0.05 to 1% by mass based on 100% by mass of the glass batch. When the amount of SnO_2 is less than 0.05%, the bubbles remaining in the molten glass become difficult to remove during the fining process. While, when the amount thereof is more than 1%, devitrification of the glass easily occurs. A preferred amount of SnO_2 is 0.1 to 0.5%.

An amount of chloride is preferably from 0.01 to 2% by mass in calculation as Cl_2 , based on 100% by mass of the glass batch, and such amount of addition provides Cl_2 in an amount of from 0.005 to 1% in the glass. When the amount of chloride is less than 0.01%, the bubbles remaining in

the molten glass become difficult to expel at the homogenizing melting. While, when the amount thereof is more than 2%, an excessively large amount of evaporation is generated, whereby the glass becomes denaturalized easily.

5 A preferred amount of chloride is 0.05 to 1% in calculation as Cl_2 , more preferably 0.05 to 0.5%, and a preferred content of Cl_2 is 0.01 to 0.5%, more preferably 0.01 to 0.3%.

In the invention, it is also possible to utilize a
10 fining agent other than those in the foregoing, such as a fluoride. Fe_2O_3 is a component also having a fining effect, but is maintained at 800 ppm or less, preferably 500 ppm or less, since a large amount of Fe_2O_3 reduces the visible light transmittance of the glass, unfavorably for
15 application in a display.

Then the prepared glass batch is molten. In case of introducing helium or neon at the melting of the glass, a suitable method can be selected from the aforementioned various methods.

20 Thereafter, the molten glass is formed into a desired shape. For application in a display, a thin sheet is formed for example by a fusion method, a down-draw method, a floating method or a roll-out method.

In this manner, there can be obtained an alkali-free
25 glass containing: by mass %,

SiO₂ in an amount of from 40 to 70%;
Al₂O₃ in an amount of from 6 to 25%;
B₂O₃ in an amount of from 5 to 20%;
MgO in an amount of from 0 to 10%;
5 CaO in an amount of from 0 to 15%;
BaO in an amount of from 0 to 30%;
SrO in an amount of from 0 to 10%;
ZnO in an amount of from 0 to 10%, and
helium and/or neon in an amount of from 0.0001 to 2
10 $\mu\text{l/g}$ (0°C, 1 atm.).

A content of helium or neon in the glass is obtained by charging (dropping) a sample of 10 to 500 mg in a Mo crucible placed in a furnace heated to 1600°C, holding the sample for 20 minutes and measuring gas, released under a
15 vacuum of 10^{-9} Torr, with a high-sensitivity rare gas mass analyzer.

EXAMPLES

In the following the alkali-free glass of the present
20 invention will be explained in detail by examples and comparative examples.

Example 1

Tables 1 and 2 respectively show Examples (samples
25 Nos. 1 to 6) of the invention and Comparative Examples

(samples Nos. 7 to 12).

Table 1

Sample	1	2	3	4	5	6
(% by mass)						
SiO ₂	60.0	54.0	56.3	58.7	62.3	64.4
Al ₂ O ₃	16.0	19.6	10.7	16.5	17.5	19.5
B ₂ O ₃	8.5	10.5	8.4	8.3	8.5	5.5
MgO	4.0	-	-	3.7	4.5	0.3
CaO	1.0	3.1	5.4	1.0	-	5.9
SrO	3.5	8.9	4.2	3.1	0.6	0.6
BaO	6.0	1.8	13.0	5.8	1.1	0.3
ZnO	1.0	-	1.3	0.9	2.7	-
(μl/g)						
He	1.980	0.982	0.498	0.004	0.132	NA
Ne	NA	NA	NA	NA	0.183	0.465
bubbles (number/100g)	< 1.0	5.2	6.5	7.5	3.5	1.3

Table 2

Sample	7	8	9	10	11	12
(% by mass)						
SiO ₂	60.0	54.0	56.3	58.7	62.3	64.4
Al ₂ O ₃	16.0	19.6	10.7	16.5	17.5	19.5
B ₂ O ₃	8.5	10.5	8.4	8.3	8.5	5.5
MgO	4.0	-	-	3.7	4.5	0.3
CaO	1.0	3.1	5.4	1.0	-	5.9
SrO	3.5	8.9	4.2	3.1	0.6	0.6
BaO	6.0	1.8	13.0	5.8	1.1	0.3
ZnO	1.0	-	1.3	0.9	2.7	-
(μl/g)						
He	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
Ne	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001	<0.00001
bubbles (number/100g)	132	155	168	212	120	295

Each sample was prepared in the following manner. At first, a batch prepared in advance for a predetermined composition corresponding to 500 g of glass was charged in a platinum crucible, which was placed in an atmospheric furnace with an air-tight structure for 4 hours at 1600°C. Then, an atmospheric gas with a He or Ne content of 95 % or higher was introduced into the furnace, and the temperature was further maintained for 30 minutes. Thereafter, glass was taken out, molded in a glass-like carbon mold and cooled. Samples Nos. 7 to 12 constituting Comparative Examples were prepared in the same conditions as above except for employing air as the melting atmosphere.

Then a number of bubbles remaining in the sample was measured with a stereo microscope of a magnification of 20

to 100 times, while the sample was held in an immersion liquid of a refractive index same as that of the glass.

A content of helium or neon in the glass was obtained by charging (dropping) a sample in a Mo crucible placed in
5 a furnace heated to 1600°C, holding the sample for 20 minutes and measuring gas, released under a vacuum of 10^{-9} Torr, with a double-collector rare gas mass analyzer (VG5400).

In these tables, NA means "not analyzed".

10

Example 2

Tables 3 to 8 show Examples of the invention (samples Nos. 13 to 43).

Table 3

Sample	13	14	15	16	17	18
(% by mass)						
SiO ₂	60.0	54.0	56.3	58.7	62.3	64.4
Al ₂ O ₃	16.0	19.6	10.7	16.5	17.5	19.5
B ₂ O ₃	8.5	10.5	8.4	8.3	8.5	5.5
MgO	4.0	-	-	3.7	4.5	0.3
CaO	1.0	3.1	5.4	1.0	-	5.9
SrO	3.5	8.9	4.2	3.1	0.6	0.6
BaO	6.0	1.8	13.0	5.8	1.1	0.3
ZnO	1.0	-	1.3	0.9	2.7	-
SO ₃	0.0004	0.0006	0.0014	0.0048	0.0096	0.0125
SnO ₂	1.0	0.6	0.3	0.15	0.1	0.05
(μl/g)						
He	1.809	0.802	0.434	0.006	0.114	NA
Ne	NA	NA	NA	NA	0.193	0.482
bubbles (number/100g)	< 1.0	< 1.0	1.4	1.5	2.5	4.5

Table 4

Sample	19	20	21	22	23
(% by mass)					
SiO ₂	58.4	56.2	54.6	59.3	62.4
Al ₂ O ₃	16.5	11.0	19.9	16.4	17.8
B ₂ O ₃	9.0	8.3	10.6	8.5	8.4
MgO	-	-	-	3.9	4.7
CaO	2.1	5.4	3.0	0.8	-
SrO	6.5	4.0	9.0	3.0	0.8
BaO	3.5	13.2	2.0	5.9	1.3
ZnO	0.5	1.5	-	1.0	3.1
Sb ₂ O ₃	0.2	0.4	1.3	1.7	2.5
SnO ₂	0.6	0.2	0.4	0.7	1.0
(μl/g)					
He	0.431	0.644	0.524	0.724	0.982
Ne	0.001	NA	NA	0.020	NA
bubbles (number/100g)	2.2	3.0	1.0	< 1.0	< 1.0

Table 5

Sample	24	25	26	27	28
(% by mass)					
SiO ₂	65.3	57.7	48.0	56.0	59.0
Al ₂ O ₃	19.8	15.7	11.0	10.5	15.0
B ₂ O ₃	5.6	8.5	14.5	5.5	10.5
MgO	0.3	3.9	-	2.0	0.5
CaO	6.2	0.8	-	3.5	4.5
SrO	0.5	3.3	-	6.0	3.0
BaO	0.4	6.1	25.0	15.0	6.0
ZnO	-	1.1	-	-	-
Sb ₂ O ₃	0.1	0.6	1.0	1.5	2.4
Cl ₂	0.06	0.3	0.2	0.4	0.5
(μl/g)					
He	0.221	0.662	0.754	0.945	1.325
Ne	NA	NA	NA	0.061	0.170
bubbles (number/100g)	3.8	1.9	1.5	< 1.0	< 1.0

Table 6

Sample	29	30	31	32	33
(% by mass)					
SiO ₂	58.0	63.0	66.0	54.0	64.5
Al ₂ O ₃	16.0	18.0	19.5	19.5	19.0
B ₂ O ₃	8.5	8.0	5.5	10.5	6.0
MgO	1.0	5.0	-	-	0.5
CaO	4.0	-	6.5	3.0	6.0
SrO	2.0	1.0	0.5	8.5	0.5
BaO	9.5	1.0	0.5	2.0	0.5
ZnO	-	3.0	0.5	-	-
Sb ₂ O ₃	0.5	0.3	0.9	0.1	1.9
SnO ₂	0.5	0.9	0.3	0.6	0.1
Cl ₂	0.5	0.3	0.1	0.1	0.1
(μl/g)					
He	0.186	0.665	0.552	0.724	0.358
Ne	NA	0.002	0.001	NA	NA
bubbles (number/100g)	1.2	< 1.0	< 1.0	< 1.0	< 1.0

Table 7

Sample	34	35	36	37	38
(% by mass)					
SiO ₂	58.4	56.2	54.6	59.3	62.4
Al ₂ O ₃	16.5	11.0	19.9	16.4	17.8
B ₂ O ₃	9.0	8.3	10.6	8.5	8.4
MgO	-	-	-	3.9	4.7
CaO	2.1	5.4	3.0	0.8	-
SrO	6.5	4.0	9.0	3.0	0.8
BaO	3.5	13.2	2.0	5.9	1.3
ZnO	0.5	1.5	-	1.0	3.1
SO ₃	0.0102	0.0068	0.0047	0.0015	0.0003
Cl ₂	0.01	0.08	0.14	0.24	0.32
(μl/g)					
He	0.412	0.512	0.489	0.701	0.893
Ne	0.001	NA	NA	0.018	NA
bubbles (number/100g)	2.2	1.3	1.1	< 1.0	< 1.0

Table 8

Sample	39	40	41	42	43
(% by mass)					
SiO ₂	65.3	57.7	48.0	56.0	59.0
Al ₂ O ₃	19.8	15.7	11.0	10.5	15.0
B ₂ O ₃	5.6	8.5	14.5	5.5	10.5
MgO	0.3	3.9	-	2.0	0.5
CaO	6.2	0.8	-	3.5	4.5
SrO	0.5	3.3	-	6.0	3.0
BaO	0.4	6.1	25.0	15.0	6.0
ZnO	-	1.1	-	-	-
Cl ₂	0.03	0.18	0.09	0.30	0.41
SnO ₂	0.05	0.1	0.3	0.4	0.9
(μ l/g)					
He	0.234	0.602	0.790	0.984	1.143
Ne	NA	NA	NA	0.048	0.151
bubbles (number/100g)	3.8	1.9	< 1.0	< 1.0	< 1.0

The samples were prepared and evaluated in the same manner as in Example 1.

- 5 As a result, the samples of the examples containing helium or neon showed 4.6 bubbles or less per 100 g and a sufficient fining effect could be confirmed.

[Advantage of the Invention]

- 10 As explained in the foregoing, the alkali-free glass of the present invention, being free from bubbles constituting defects in display, is suitable for a transparent glass substrate for a display, particularly for a transparent glass substrate for a liquid crystal display.
- 15 In addition to the application for the liquid crystal

display, it is applicable as a glass substrate for other flat panel displays such as an electroluminescent display, a cover glass for image sensors such as a charge-coupled device, an equal-size proximity solid-state image pickup
5 device or a CMOS image sensor, or a glass substrate for a hard disk or a filter.

[Designation of Document] Abstract

[Abstract]

[Problem] A subject for the invention is to provide an alkali-free glass which is capable of reducing or totally
5 eliminating As_2O_3 and which has fewer bubble inclusion than that in the prior technology.

[Means for Solving the Problem] The invention relates to an alkali-free glass which comprises, by mass %, SiO_2 in an amount of from 40 to 70%; Al_2O_3 in an amount of from 6 to
10 25%; B_2O_3 in an amount of from 5 to 20%; MgO in an amount of from 0 to 10%; CaO in an amount of from 0 to 15%; BaO in an amount of from 0 to 30%; SrO in an amount of from 0 to 10%; ZnO in an amount of from 0 to 10%, and helium and/or neon in an amount of from 0.0001 to 2 $\mu\text{l/g}$ (0°C , 1 atm.).
15 In the invention, "alkali-free" means that alkali metal oxides (Li_2O , Na_2O , and K_2O) are present in an amount of 0.2% by mass or less.

[Selected Drawing] None